The Thesis Committee for Christopher Guy Cacciatore
Certifies that this is the approved version of the following thesis:

Interpreting the Difference in Magnitudes of PETM Carbon Isotope Excursions in Paleosol Carbonate and Paleosol Organic Matter: Oxidation of methane in soils versus elevated soil respiration rates

APPROVED BY
SUPERVISING COMMITTEE:

Supervisor:

Daniel O. Breecker, Supervisor

Timothy M. Shanahan

Jennifer M. Cotton

Interpreting the Difference in Magnitudes of PETM Carbon Isotope Excursions in Paleosol Carbonate and Paleosol Organic Matter: Oxidation of methane in soils versus elevated soil respiration rates

by

Christopher Guy Cacciatore, B.A.; B.S. Bioch

Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Geological Sciences

The University of Texas at Austin

May 2016

Acknowledgements

I would like to thank Ji Shunchuan, Tim Shanahan and Jennifer Cotton for guidance and insight. And of course, thank you to my family, friends and Alexa for their support throughout the years.

Abstract

Interpreting the Difference in Magnitudes of PETM Carbon Isotope Excursions in Paleosol Carbonate and Paleosol Organic Matter: Oxidation of methane in soils versus elevated soil respiration rates

Christopher Guy Cacciatore, MSGeoSci

The University of Texas at Austin, 2016

Supervisor: Daniel O. Breecker

Abstract: The Paleocene-Eocene Thermal Maximum (PETM) was a rapid global warming event at ~56 Ma that was driven by a rapid release of carbon into the ocean-atmosphere system. The most recognizable feature marking the PETM in the rock record is a negative carbon isotope excursion (CIE) recorded in organic carbon and calcium carbonates deposited in both marine and terrestrial environments. Differences among excursion magnitudes (ΔCIE) exist between marine and terrestrial proxies, and between carbonates and organic carbon. We evaluated the plausibility of two hypothetical mechanisms behind the observed ~ 1.9‰ difference between the magnitude of the CIE as recorded by paleosol carbonate and paleosol organic matter ($\Delta CIE_{pc\text{-}som}$). Specifically, we test whether 1) oxidation within soils of isotopically light methane or 2) increases in soil respiration rates are plausible explanations for the observed ΔCIE. A production-diffusion model used to simulate carbon isotope compositions of soil CO_2 and paleosol carbonates is coupled with a box model that constrains methane flux from hydrates into atmosphere. The box model simulates atmospheric CO_2 concentrations, the $\delta^{13}C$ values of atmospheric CO_2 and of plants, and the methane flux into soils, which are all used in the production-diffusion model to simulate the $\delta^{13}C$ value of paleosol carbonate. Given conservative prior

distributions for model inputs grounded in previous empirical studies, model output demonstrates that oxidation of atmospheric methane in soil pore space is unlikely to cause the $\Delta CIE_{pc\text{-}som}$ even for rapid methane release rates. However, increased respiration rates during the PETM could explain the observed ΔCIE, with a minimum approximate doubling of respiration rates required to reproduce a $\Delta CIE_{pc\text{-}som} \geq 2‰$.

Table of Contents

I: INTRODUCTION & BACKGROUND 1

a) Carbon injection and a global $\delta^{13}C$ excursion.....1

b) Controls on the $\delta^{13}C$ values of pedogenic carbonates 3

c) Effects of methane on soil CO_2, respired CO_2, organic matter, and carbonates 4

d) Terrestrial CIEs in the Geologic Record 5

II: METHODS 9

a) Model Description.....9

b) Model Assumptions.....12

i) Intensity and duration of Carbon Injection Scenarios 13

ii) Oceanic and Atmospheric Oxidatin of Dissociated Methane 15

iii) Concentration and $\delta^{13}C$ range for PETM Atmospheric CO_2.....16

iv) Soil Respiration Rates, $\delta^{13}C$ values of Methane, and $\delta^{13}C$ values of SOM 17

v) Average Depths of Production.....18

vi) Effects of Methanogenic and Methanotrophic Activity 19

III: SENSITIVITY TESTS AND RESULTS 21

a) Part I: Effects of Atmospheric Methane Oxidation in Soil on $\delta^{13}C_{pc}$.....21

b) Part II: *Effects of Elevated Respiration Rates on* $\delta^{13}C_{ped}$ 25

IV: CONCLUSIONS 28

V: REFERENCES 34

I: Introduction & Background

Carbon injection and a global $\delta^{13}C$ *excursion*

The Paleocene-Eocene Thermal Maximum (PETM) was a rapid global warming event at 55.9 Ma driven by a rapid release of carbon into the ocean-atmosphere system (Zachos et al. 2001). The PETM is a potential analog for understanding the consequences of modern atmospheric CO_2 rise. The comparison is not without discrepancy, however, as PETM warming occurred in an already warm 'greenhouse' period. Additionally, current rates of total carbon emission exceed rates at the onset of the PETM (Zeebe et al. 2016, Zeebe et al. 2009, Stocker et al. 2013). Perhaps the most ubiquitous feature marking the PETM in the rock record is a negative carbon isotope excursion (CIE) that is recorded in organic carbon and calcium carbonates deposited in both marine and terrestrial environments. Differences in the CIE magnitude exist both between marine and terrestrial proxies, and between organic carbon and calcium carbonate (Bowen et al. 2004, Hesselbo et al. 2007, Abels et al. 2012, Tipple et al. 2011, Cotton & Sheldon 2015). Terrestrial proxies are characterized by larger magnitude negative excursions compared to marine proxies; on average $\Delta CIE_{terrestrial\text{-}marine} \sim -1.9‰$, (McInerney & Wing 2011, Schubert & Jahren 2013). An increase in the magnitude of carbon isotope fractionation during photosynthesis in C_3 land plants with increasing atmospheric pCO_2 (Schubert and Jahren 2012) may explain the $\Delta CIE_{terrestrial\text{-}marine}$, reflecting an increase in atmospheric pCO_2 during the PETM (Schubert & Jahren 2013). This mechanism does not explain the differences between the magnitude

of the excursion recorded in paleosol carbonates and paleosol organic matter ($\Delta CIE_{pc\text{-}om}$), because plant $\delta^{13}C$ values control the $\delta^{13}C$ values of both of these carbon reservoirs and thus an excursion in plant $\delta^{13}C$ values should result in $\Delta CIE_{pc\text{-}om} = 0$, all else being equal (Bowen et al. 2004). Although negative carbon isotope excursions are observed in both paleosol carbonate sand paleosol organic carbon, the magnitude of CIE_{pc} is on average 1-2‰ greater than CIE_{om} (i.e. $\Delta CIE_{pc\text{-}om}$ = -1 to -2 ‰). Elevated rates of soil respiration have been suggested to explain the observed $\Delta CIE_{pc\text{-}om}$ (Sheldon and Cotton 2015). Here we evaluate this mechanism quantitatively. We also evaluate a mechanism suggested here for the first time: oxidation in soils of methane released into the atmosphere during the PETM. In particular, we attempt to assess whether elevated atmospheric methane levels could have resulted in sufficiently high methane oxidation in soils (producing isotopically light soil pore space CO_2) to shift $\delta^{13}C_{pc}$ to more negative values, while having negligible effects on $\delta^{13}C_{om}$. Such an effect might explain rapid recovery from the pre onset excursion (POE) observed in paleosol carbonates in core recovered from the Bighorn Basin (Bowen et al 2015), because the residence time of methane in the atmospheric is so short (Jacob 2000). Quantifying these effects is important for accurate interpretation of the paleosol record of the PETM, including the use of paleosols to: 1) reconstruct changes in terrestrial environments and atmospheric pCO_2 and 2) constrain carbon injection scenarios.

The global carbon isotope excursion during the PETM, coupled with evidence of widespread carbonate dissolution (Zachos et al. 2005) and shoaling of the calcite

compensation depth (Kenneth and Stott 1991), suggest a large injection of ^{13}C-depleted C into the ocean-atmosphere system. The model used here works under the assumption that the source of ^{13}C-depleted carbon came primarily from dissociation of methane hydrates along continental shelves, which is the most widely accepted theory for initial perturbation at the onset of the PETM (Dickens 1995, Dickens 2003). Methane hydrate dissociation was likely triggered by thermal instability resulting from changes in ocean circulation occurring on 1000 year timescales (Darnell et al. 2015, Dickens 2001). If atmospheric methane levels were substantially elevated, methane that diffuses into soil pore spaces may have fueled methanotrophy in soils, contributing isotopically light carbon to soil CO_2 and thus paleosol carbonates.

Controls on the $\delta^{13}C$ values of pedogenic carbonates

Soil organic matter (SOM) consists primarily of plant matter and ultimately incorporates fungi and bacteria cellular tissue as it stabilizes (Rumpel & Kogel-Knabner 2009). SOM $\delta^{13}C$ values ($\delta^{13}C_{om}$) are controlled by $\delta^{13}C$ values of atmospheric CO_2, aridity and possibly the concentration of atmospheric CO_2 (Schubert and Jahren 2012). Pedogenic carbonates on the other hand, derive carbon from CO_2 in soil pore space. Pedogenic carbonate $\delta^{13}C$ values are therefore controlled by $\delta^{13}C$ values of CO_2 in the soil pore space and temperature. Soil pore space CO_2 is a mixture between atmospheric CO_2 and CO_2 respired in the soil. This includes all sources of respiration in soil, such as root respiration and microbial decomposition. The $\delta^{13}C$ values of CO_2 in the soil pore spaces are thus controlled

by the relative concentrations and the $\delta^{13}C$ values of these two end members: soil respired CO_2 (S(z), $\delta^{13}C_{resp}$) and atmospheric CO_2 ($[CO_2]_{atm}$, $\delta^{13}C_a$). This is the central tenant behind the paleosol carbonate CO_2 proxy (Cerling 1991) visualized in Figure 1. For example, as S(z) increases, $\delta^{13}C_{pc}$ decreases because soil respired CO_2 has lower $\delta^{13}C$ values than atmospheric CO_2. Alternatively, as $[CO_2]_{atm}$ increases, $\delta^{13}C_{pc}$ increases. This study analyzes two potential changes in conditions that may have occurred during the PETM and caused depletion of $\delta^{13}C_{pc}$ independently of $\delta^{13}C_{OM}$: 1) During the PETM, oxidation of methane in soil pore space may have provided an additional source of ^{13}C-depleted carbon ($\delta^{13}C_{ox\text{-}meth}$), decreasing $\delta^{13}C_{soil\text{-}CO2}$ and ultimately $\delta^{13}C_{pc}$. 2) Increasing respiration rates throughout the PETM may have increased S(z), again decreasing $\delta^{13}C_{soil\text{-}CO2}$ and $\delta^{13}C_{pc}$

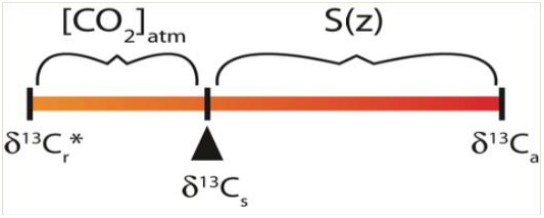

Figure 1: A graphical representation of CO_2 mixing in soil pore spaces. The $\delta^{13}C$ value of CO_2 in the soil pore space is dictated by concentration and $\delta^{13}C$ values of respired and atmospheric CO_2. The $\delta^{13}C_r$* is the $\delta^{13}C$ value of respired CO_2 corrected for diffusion (Breecker et al. 2010)

Effects of methane on soil CO_2, respired CO_2, organic matter, and carbonates

A large increase in atmospheric methane during the PETM may have been sufficient to trigger a negative CIE in paleosol carbonates. The location of methane oxidation is crucial. If the methane is oxidized in the atmosphere or ocean, the light carbon would shift the $\delta^{13}C$ values of atmospheric CO_2, plants, soil organic matter, soil CO_2 and thus pedogenic

carbonates. $\Delta CIE_{pc\text{-}om}$ would be close to zero in this case. However, oxidation of atmospheric methane in soils might substantially shift the $\delta^{13}C$ value of soil CO_2 and thus paleosol carbonates. Decomposition of methanotrophs would also contribute depleted ^{13}C to the soil organic matter pool. Overall, the contribution of isotopically light carbon from methane dissociation to soil organic matter is relatively small compared to the size of the total carbon pool when compared to the contribution to soil CO_2 (Rosley et al. 1997). In this study, we used a model to quantify the response of $\delta^{13}C_{om}$, $\delta^{13}C_{pc}$ and by consequence $\Delta CIE_{pc\text{-}om}$ to soil methane oxidation.

Terrestrial CIEs in the Geologic Record

The model attempts to quantify the factors that can reproduce the $\Delta CIE_{pc\text{-}om}$ recorded at the PETM. Constraints on the magnitude of $\Delta CIE_{pc\text{-}om}$ come from three locations. The Bighorn Basin, Wyoming has the highest resolution paleosol $\delta^{13}C$ data for the PETM. Previous studies analyzed paleosol samples to obtain $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ records of 68 samples spanning the entire PETM, resulting in an average $\Delta CIE_{pc\text{-}om}$ of -2.8‰ (Bowen et al. 2001, Bowen et al. 2015). A second record from Ax Handle Canyon, Utah (31 samples, Bowen and Bowen 2008) and a third from the Tendruy section near Lleida, Spain (51 samples, Schmitz and Pujalte 2003, Magioncalda et al. 2004) indicating average $\Delta CIE_{pc\text{-}om}$ values of -1.3 and -3.2 respectively. The averaged excursion magnitudes, are -5.5‰ for $\delta^{13}C_{pc}$ compared to -3.5‰ for $\delta^{13}C_{om}$ resulting in an average $\Delta CIE_{pc\text{-}om}$ across sites of -2.3 We

attempt to simulate this average $\Delta CIE_{pc\text{-}om}$ using a carbon cycle box model coupled to a soil CO_2 production-diffusion model.

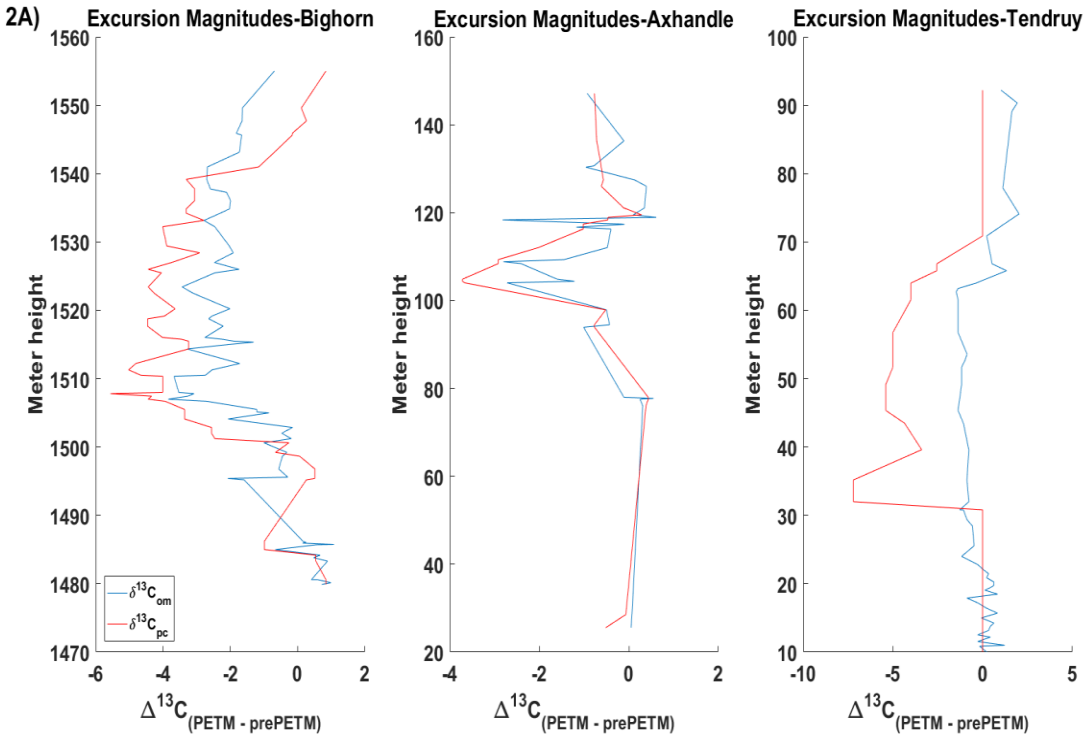

Figure 2: See next page for full caption

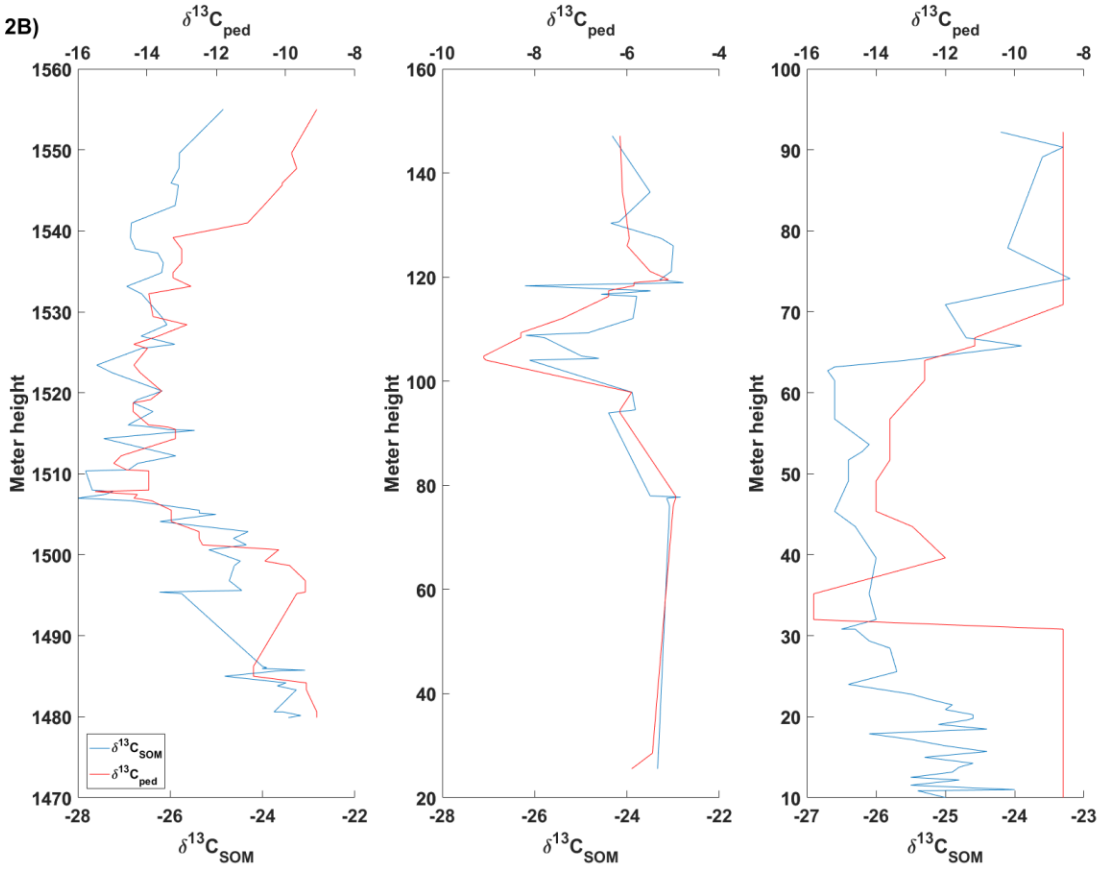

Figure 2: The $\Delta CIE_{pc\text{-}om}$ is represented by the difference between the red and blue lines in 2a. The raw excursions for SOM and pedogenic carbonate are shown below in 2b. Data from (Bowen & Bowen 2008, Schmitz and Pujalte 2003, Magioncalda et al. 2004, Bowen et al. 2015, Sheldon & Cotton 2015)

A smaller, but nonetheless substantial negative CIE that predates the onset of the PETM (the pre onset excursion or POE) is observed in paleosol carbonates in the Bighorn Basin (Bowen et al 2015). The POE is also marked by a rapid recovery to near prePETM levels, which is difficult to explain as carbon is recycled through the ocean-atmosphere system relatively slowly. A rapid recovery is consistent with the hypothesis that elevated methane levels are the primary cause of the POE. Elevated methane levels and subsequent oxidation

in soil should exist primarily at the onset of carbon injection, but would rapidly subside as soon as methane levels subside given the short residence time of atmospheric methane (Cicerone & Oremland 1988).

II: Methods

Model description

An annual rate of methane release is simulated for each run by sampling from a Gaussian distribution of potential values. Ranges of values for the prior are discussed in model assumptions. The released methane is subsequently oxidized in the ocean and atmosphere. As the methane concentration in the atmosphere increases, the rate of oxidation in the atmosphere increases. CO_2 from oxidation of methane in the atmosphere mixes with ambient CO_2 in the atmospheric reservoir, which influences the atmospheric component of soil CO_2. Moreover, increases in methane concentration in the atmosphere result in an increase in methane flux into soils and thus methane oxidation rates in the soil pore space. These steps are illustrated in Figure 3.

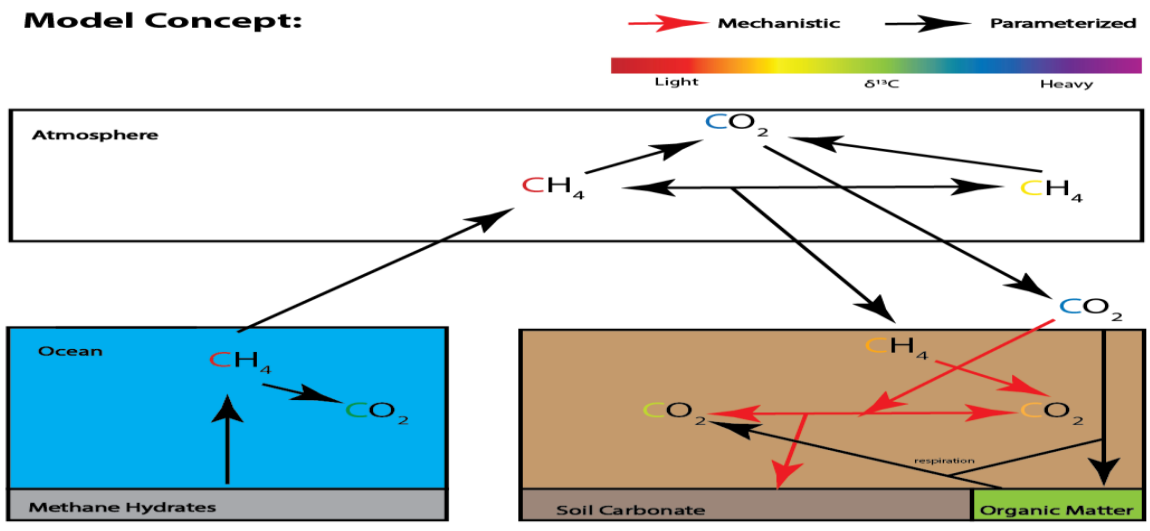

Figure 3: Conceptual visualization of model. Parameterized interactions are based on building probability distributions with minimum and maximum values grounded in findings from other studies. Mechanistic processes are calculated based on physical governing equations for the processes

For both sensitivity tests, the first simulation in each paired run is a null state in which the rate of methane oxidation in soil is set to 0. In this case, values of $\delta^{13}C_{soil\text{-}CO2}$ can be calculated using the following equations substituted with values relevant for $^{12}CO_2$ and $^{13}CO_2$ (Cerling 1984, Cerling 1999):

(1) $\frac{\partial C_s}{\partial t} = D_{soil} \frac{\partial^2 C_s}{\partial z^2} + \phi_s(z)$

(2) $D_{soil} = D_{CO2-air} \varepsilon \rho$

(3) $\phi_s(z) = \phi_s(z = 0) e^{-(\frac{z}{cdepth})}$

where C_s is the concentration of soil CO_2, D is the diffusion coefficient of CO_2 through a particular medium, ε is the free-air porosity, ρ is the tortuosity factor, and ϕ is the depth dependent CO_2 production rate. This production-diffusion model is illustrated in Figure 3 by the mechanistic flow chart in the soil section. Values of these variables and the associated uncertainties, discussed below, are considered using the Monte Carlo approach for each simulation.

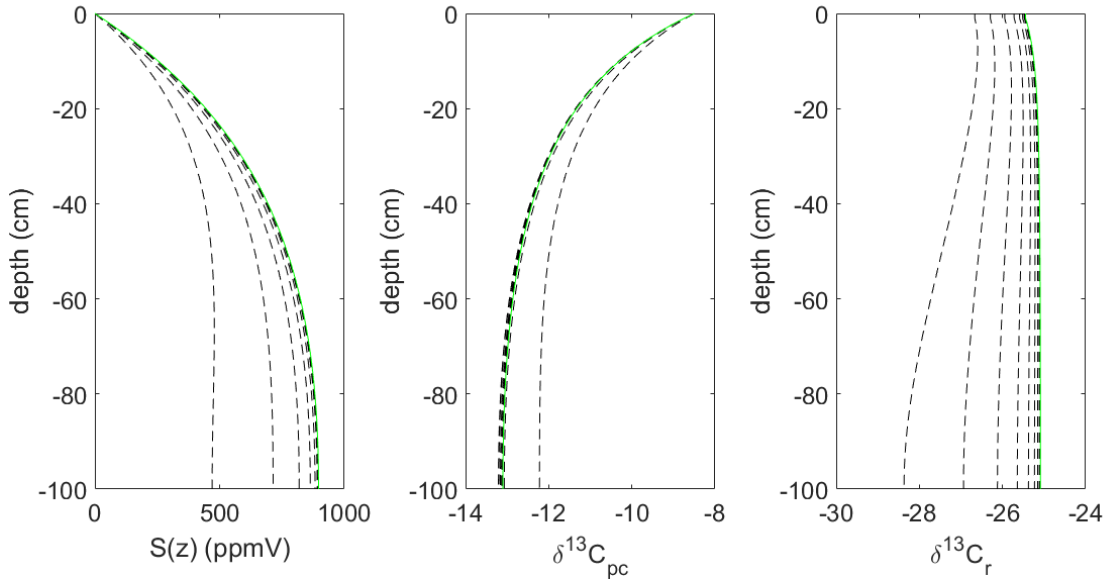

Figure 4: Dashed lines represent the change in respiration or isotopic profile at depth through time as calculated by the governing equations for the production-diffusion model. The green line represents the point at which steady-state is reached.

The production rate (ϕ_s) is calculated as a function of depth via equation 3. D_{soil} varies with depth but is held constant through time. $D_{CO2\text{-}air}$ is held constant at 0.114 cm^{-2} s^{-1}. From the initial conditions of atmospheric air CO_2 filling soil pore spaces the model steps through time until steady state soil CO_2 $\delta^{13}C$ values are achieved. When the difference between calculated values of $\delta^{13}C_{resp}$ is insignificant between timesteps (<0.01‰ after 24 hours) at a depth of 95cm, the system is considered to be at steady-state.

The diffusion of ^{13}C and ^{12}C throughout the soil profile is calculated until steady state is reached. The steady state values of $\delta^{13}C_{soil}$ and $\delta^{13}C_{resp}$ are recorded for each simulation and interpreted as $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ respectively. The CIE_{pc} is calculated using the $\Delta^{13}C_{pc}$ between paired runs. The CIE_{om} is calculating using the $\Delta^{13}C_{om}$ between paired runs, though the values are negligible (CIE_{om} ~ 0) between runs given the independent variables (S(z)

and soil pore space methane oxidation rate). For the first Monte Carlo sensitivity test, hereon referred to as $MC_{meth\text{-}ox,}$ the first simulation in each paired run represents the formation of pedogenic carbonate in a prePETM state approximated by zero oxidation of methane in soil pore space. The second simulation in each paired run maintains all of the same inputs as the null (first simulation), but uses a nonzero methane oxidation rate (i.e. the flux of methane from the box model into the production-diffusion model becomes significant). From there, $\Delta CIE_{pc\text{-}om}$ is calculated as $CIE_{pc} - CIE_{om}$ (which in most cases is approximately CIE_{pc}). In the second Monte Carlo sensitivity test, hereon referred to as MC_{resp}, a change in respiration rate is induced between paired runs, again with each even simulation representing formation during the PETM via an increased respiration rate and a distribution for atmospheric CO_2 levels set at a higher range discussed in detail under model assumptions. Besides changes in the priors for atmospheric CO_2 concentrations and respiration rates, all other variables are kept constant between pairs. Methane oxidation in soil pore space is not simulated in any runs during the second sensitivity test (MC_{resp}). For both tests, the $\Delta^{13}C_{pc}$ is representative of a $\Delta CIE_{pc\text{-}om}$, as any changes to $\delta^{13}C_{om}$ between pairs are transferred to the carbonate via soil-respired CO_2.

Model Assumptions

The values of input variables are based on the findings of previous empirical and theoretical studies of the PETM as discussed in this section. Uncertainty in simulated values of $\Delta CIE_{pc\text{-}om}$ is evaluated by assigning probability distributions (priors) to each input variables. This section is intended to demonstrate conservative estimations of unknowns in an effort to

verify the robustness and broad inclusivity of model output. Conservative estimations require distributions broad enough to avoid false negatives. In other words, that the model does not miss any potential effects of methane oxidation in soil nor in any change in respiration rates, but is still grounded in constraints from previous studies. The potential for false positives is negligible for methane oxidation tests, but is assessed for respiration increases later in the discussion. Priors are discussed here in order of model sensitivity, which is a function of both uncertainty of input variables and the weighted effect of the parameter relative to other variables.

Intensity and duration of Carbon Injection Scenarios

The first prior is grounded in estimations of the rate of carbon release from methane clathrate dissociation during the PETM. This is the most widely discussed triggering mechanism for the CIE (Dickens 1995, Zeebe 2016, Zachos et al. 2008, Jones et al. 2010, Sluijs et al. 2007). Nearly every study explaining the PETM with methane hydrate dissociation suggests release on the scale of 1-10 exagrams (10^{18} grams) of carbon (McInerney & Wing 2011). Proposed carbon injection totals include 4.3 Exg (Diefendorf et al. 2010), 6.9Exg (Panchuk et al. 2008), 3.0Exg (Zeebe et al. 2009), which are based on fitting carbon cycle model predictions to observations. Specifically, simulated carbonate compensation depth (CCD) in the Atlantic is consistent with observations of input scenarios between 1.5-4.5 Exg while initial input is constrained to a maximum of 3 Exg given CCD shoaling in the Pacific (Zeebe 2009). A more recent study modeled carbon

injection of 2500-4500PgC with varied release times and determined only injection scenarios with a 4000yr release or longer can reproduce $\delta^{13}C$ and $\delta^{18}O$ lag/lead timing in foraminiferal records (Zeebe et al. 2010, Zeebe et al. 2016).

Total carbon injection is a function of both the rate of carbon release and the number of pulses. Assuming 1-10 exagrams Exg of methane is released as a single constant rate pulse, if the total carbon mass is released in 10,000 years, then injection rates are on the scale of 0.1 PgC/yr. Similarly, if the total mass is released in 100 years, then the injection rates are on the scale of 10 PgC/yr. While a multiple pulse carbon release is more consistent with observations in both marine and terrestrial proxies (Dickens 2001, Bowen 2004, Bowen 2010), the simplified single pulse model provided in this study nonetheless provides a good benchmark for the effect of different magnitudes and timings of pulses on CIEs as recorded in paleosol carbonates by ensuring the methane oxidation rate in soil scales with methane injection into the atmosphere. The methane release rate is important for the simulations in this study because given the short residence time of methane in the atmosphere, it is more likely that high methane in soil pore space would occur in cases of shorter, more intense input of methane into the atmosphere. Thus, as a sensitivity test, the distribution for the methane injection flux is first set as a Gaussian with mean $3e^{16}$ gC/yr and $\sigma = 1e^{16}$ to simulate an injection of ~3000PgC over 100 years. A total injection of ~3000PgC is also consistent with a minimum calculation for carbon release from heat propagation calculations of present-day gas hydrate reservoirs that would be susceptible to hypothesized increases in bottom water temperature (Kvenvolden 1998, Dickens 2003).

The distribution of carbon release rates is then set to simulate the 1000 and 10000 year input scenarios by keeping the total injected mass constant, but increasing the mean release rates (means of $3e^{15}$ gC/yr and $3e^{14}$ gC/yr respectively), which are more consistent with sedimentation and carbon cycle box modeling (Bowen et al. 2015, Zeebe et al. 2016).

Oceanic and Atmospheric Oxidation of Dissociated Methane

The estimation of methane injection into the atmosphere used in the model takes into account an estimate that two-thirds of the methane released from clathrates was oxidized in the ocean (Schmidt & Shindell 2003). The remaining 1/3 emitted to the atmosphere has a short residence time (~14 years) as OH^- radicals convert methane to CO_2 in the upper troposphere, and to a lesser extent the stratosphere (Cicerone & Omerland 1988). Under modern conditions, approximately 95% of methane emitted to the atmosphere is oxidized in the atmosphere and 5 to 7% is oxidized in soils (Ehhalt & Schmidt 1978, Dorr et al. 1993). We use a conservatively high (given our result) estimate that 10% of the methane injected into the atmosphere is oxidized in soils. Given the global nature of carbon isotope excursions in soil carbonate, the model also assumes a uniform methane oxidation across the land surface, a total of 1.21×10^8 km^2 (Jackson et al. 1997). Uncertainties in this fraction are overwhelmed by uncertainty in methane injection rates.

Concentration and $\delta^{13}C$ range for PETM Atmospheric CO_2

The second prior is a determination of plausible pCO_2 levels throughout the PETM. Any differences between $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ as a result of increases in soil respiration rates and porespace methane oxidation are more likely to occur if atmospheric pCO_2 was lower. Because $\delta^{13}C_{pc}$ is a function of the relative fractions of atmospheric CO_2 and respired CO_2 in the soil porespace, low atmospheric CO_2 results in a $\delta^{13}C_{pc}$ more easily influenced by elevated soil respiration rates or oxidation of methane in soils. To be conservative, we use the lowest plausible values of $pCO_{2\ atm}$ before the onset of the PETM as a prior in both sensitivity tests, as it simultaneously maximizes any effect of methane oxidation in the first sensitivity test ($MC_{meth\text{-}ox}$), while minimizes the simulated CIE magnitudes in the second sensitivity test (MC_{resp}). Paleocene pCO_2 estimates range from 200ppm – 2,800 ppm and changes through the PETM, though many proxies suggest values of ~400ppm at the onset (Breecker et al. 2010, Hilting et al. 2008, Pearson & Palmer 2000, Royer et al. 2007). Assuming the lower prePETM pCO_2 value of ~400ppm, an increase to ~1600ppm corresponds to a 4.3 Exg injection over the total duration of the PETM. However, many models have suggested that the prePETM baseline should have been higher than modern levels (Zachos 2009, Pagani et al. 2006). For example, a pre-onset range of 750-1000ppmv was used in recent studies using the Grid Enabled Integrated Earth system (GENIE) and LOSCAR models (Zeebe et al. 2012, Zeebe et al. 2016). As a conservative estimate we use a range of 400 to 1000ppm for $pCO_{2\ atm}$ for all simulations of prePETM pedogenesis. For PETM simulations, a range of 500-1500ppm is used as a prior for potential increase of

$pCO_{2\ atm}$ relative to the sampled prePETM $pCO_{2\ atm.}$ These ranges are not only consistent with methane hydrate dissociation hypotheses, but also concentrations calculated using GENIE model for late Paleocene ocean alkalinity, dissolved inorganic carbon and seafloor carbonate carbonate (Panchuk et al. 2008), and simulated shoaling of the calcium carbonate compensation depth in the Pacific (Zachos et al. 2009).

Providing a distribution of possible $\delta^{13}C_a$ values of CO_2 is difficult, as many efforts to elucidate differences between proxy CIEs are done in part to determine which most accurately corresponds to atmospheric CIE magnitudes. Suggested PrePETM $\delta^{13}C_a$ values are estimated at -5‰ (Tipple et al. 2010) to -9‰ (McInerney and Wing 2011). Lower $\delta^{13}C_a$ values result in smaller $\Delta CIE_{pc\text{-}om}$ resulting from methane in soil pore space. To broadly include all feasible scenarios where methane oxidation or increased respiration in soils may reproduce the observed $\Delta CIE_{pc\text{-}om}$, it is important to include the heaviest possible values for $\delta^{13}C_{a.}$ The range for the $\delta^{13}C_a$ prior does not affect the calculated $\Delta CIE_{pc\text{-}om}$ due to increases in soil respiration rates as simulated in the second sensitivity test (MC_{resp}). This is because the value of $\delta^{13}C_a$ is held constant between paired runs and $\delta^{13}C_{resp}$ is calculated from $\delta^{13}C_a$. Thus, the model uses a left skewed Gaussian distribution ranging from -4 to -12‰.

Soil Respiration Rates, $\delta^{13}C$ values of Methane, and $\delta^{13}C$ values of SOM

Uncertainty in these distributions, as a result of evidential confidence in their range and/or relatively small effect on model output, is less critical. The respiration rate is set as a flat distribution between 0.1 – 10 mmol/m^2/h (Brook et al 1983, Raich and Potter 1995) for the first sensitivity test ($MC_{meth\text{-}ox}$) which tests the effects of methane oxidation in soil. This is also used as the lower range for the second sensitivity test (MC_{resp}) which tests the effects of increased respiration rates. The range of elevated respiration rates considered (10 - 20 mmol/m^2/h) is well within the range of modern soils during dry months (Franzluebbers et al.2002) when pedogenic carbonate likely forms (Breecker et al 2009). The $\delta^{13}C$ value of methane originating from methane clathrate deposits can be anywhere in the range of -70 to -55 ‰ (Dickens 2011, Bowen 2015). More negative values increase the effect of methane oxidation on $\Delta CIE_{pc\text{-}om}$, so it is vital to ensure the most negative values reasonable are considered. The distribution used is thus, a flat distribution from -70 to -55 ‰. Finally, the $\delta^{13}C$ values of SOM have been measured across the three sites and we use a flat distribution from -27 to -20‰ to approximate their distribution.

Average Depths of Production

The average depth of CO_2 production is defined as the depth above which half of the total CO_2 flux into the soil from respiration occurs. A separate average depth is used to characterize the depth distribution of methane oxidation. Average depths of CO_2 production are experimentally determined depths meant to characterize rates of CO_2 from respiration in a particular ecosystem. To maximize the fraction of soil CO_2 from methane

oxidation, a conservative prior must contain the shallowest possible average depths for SOM oxidation and the deepest possible depths for oxidation of atmospheric methane that are still consistent with experimental studies. *In situ* measurements of CO_2 production depths in modern forest soils suggest average depths on the order of 10-20cm (Gaudry et al. 1990, Dorr & Munnich 1990), with desert soils having even deeper characteristic depths of up to 60cm (Breecker et al. 2012). *In situ* studies of methane production suggest a potential range of 5-40cm (Schnell & King 1994). Based on the assumption that the characteristic depth of both CH_4 and CO_2 during the PETM were similar to modern, the characteristic depths are estimated as uniform distributions at 1– 40cm and 5-40 cm for CO_2 and CH_4 respectively.

Effects of Methanogenic and Methanotrophic Activity

Nearly all semi-arid to arid soils in which pedogenic carbonates form are net methane sinks (Potter et al. 1996), oxidizing atmospheric methane at rates of nearly 200μg CH_4 m^{-2} h^{-1} (Strieg et al. 1992). Given that fluxes from oxidization of atmospheric methane are four to five orders of magnitude less than respiration rates observed in modern environments (Franzluebbers et al. 2002), the effect of methane oxidation on $\delta^{13}C_{pc}$ is generally ignored (excluding this study where we are testing the additional response to elevated methane levels during the PETM). Significant methanogenesis is generally limited to soils in wetland and marsh soils. Although there are some reports of simultaneous methane production and consumption in well drained upland soils and in semi-arid ecosystems like

tropical savannas (Poth et al. 1995, Keller & Reiners 1994), we did not consider methanogenesis in the soil in our simulations. Methanotrophic activity drives oxidation in methane in soils, but is assumed to not affect $\delta^{13}C_{om}$. This assumption is assessed in detail in the discussion.

III: Sensitivity Test Results and Discussion

Part I: Effects of Atmospheric Methane Oxidation in Soil on $\delta^{13}C_{pc}$

The first sensitivity test ($MC_{meth\text{-}ox}$) treats the prior for CO_2 flux from methane dissociation as an independent variable. To simulate an injection of ~3000PgC over 100 years, 1000 years and 10,000 years respectively, three sets of 1000 paired simulations (2000 total) were run using Gaussian distributions for carbon injection totals with: μ = 3e16 gC/yr and σ = 1e16, μ = 3e15 gC/yr and σ = 1e15, and μ = 3e14 gC/yr and σ = 1e14 for each respective set. Results from each set of simulations are shown in figures 5A-C.

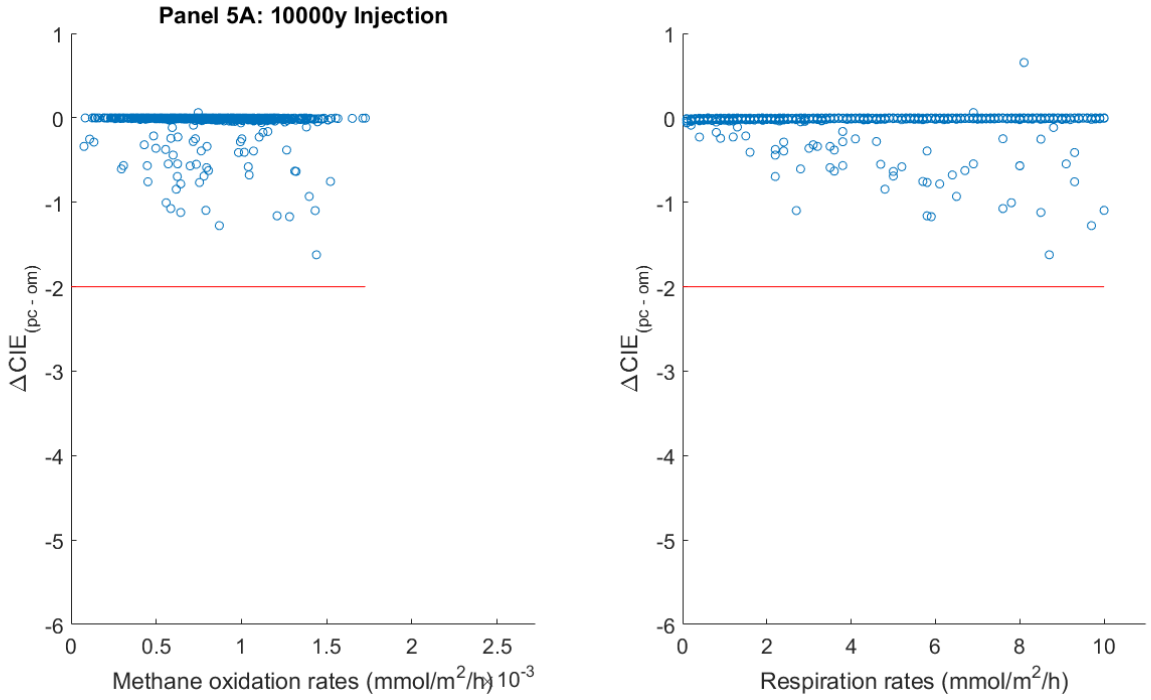

Figure 5: See next page for full caption

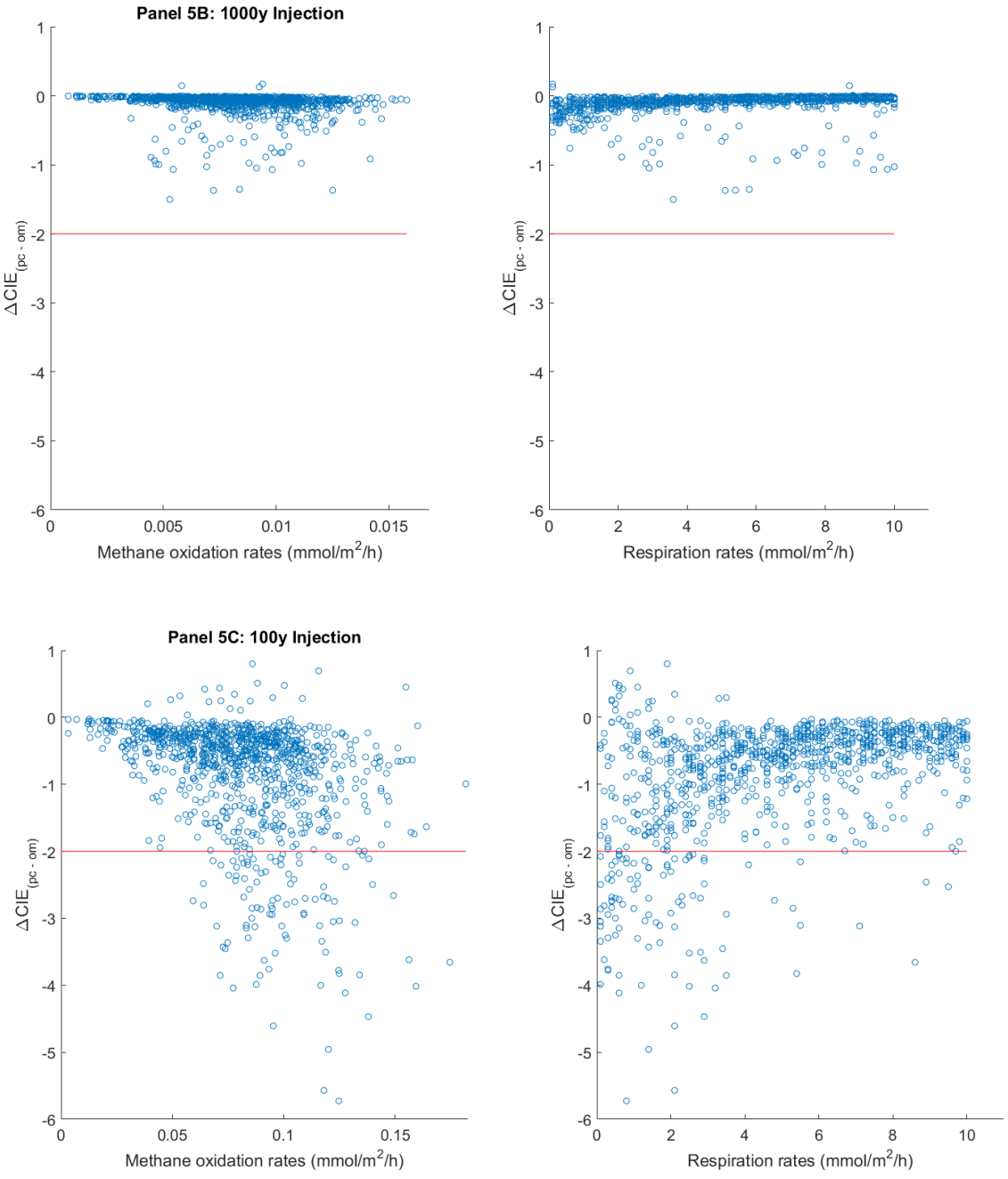

Figure 5: Simulated values of $\Delta CIE_{pc\text{-}om}$. The red line indicates the observed $\Delta CIE_{pc\text{-}om}$ at ~2‰. Oxidation of methane in soil is only sufficient as the primary mechanism for $\Delta CIE_{pc\text{-}om}$ when respiration rates are low, and still only occurs in <10% when carbon injection is on the order of magnitude of 100 years

Scatter plots illustrate the $\Delta CIE_{pc\text{-}som}$ between paired runs at various soil respiration rates and porespace methane oxidation rates. $\Delta CIE_{pc\text{-}om}$ values approach zero at higher respiration rates and lower methane oxidation rates. The $\delta^{13}C_{soil\text{-}CO2}$ is a function of mixing between $\delta^{13}C_a$, $\delta^{13}C_{resp}$ and the $\delta^{13}C_{ox\text{-}meth}$. With less respired CO_2, the carbon from oxidation of methane in the soil porespace and the associated $\delta^{13}C_{ox\text{-}meth}$ signature have a greater relative contribution to the $\delta^{13}C_{soil\text{-}CO2}$ and thus there is a stronger excursion signal resulting from incorporation of methane carbon during simulation of low respiration rates. Moreover, $\Delta CIE_{pc\text{-}om}$ is larger when methane injection into the atmosphere is faster (i.e. it occurs over a shorter time interval, compare figures 5A, 5B and 5C). Thus, when methane oxidation is high and respiration rates are low, ~3000PgC injection over 100 years results in the most delivery of methane to soil pore space relative to other simulation sets. Despite the higher elevated methane levels when simulating a 100-year injection, only ~10% of the 1000 paired runs result in a $\Delta CIE_{pc\text{-}som}$ consistent with observed levels. Perhaps more telling is that none of the 1000 paired simulations of a ~3000PgC injection over 1000 years, let alone over 10,000 years, reach a $\Delta CIE_{pc\text{-}som} \geq$ than the -2‰ threshold. Assuming a constrained maximum release rate of 1.1 Pg C y^{-1}, simulated releases ~1000 years (i.e. normally distributed around a 3.0 Pg C y^{-1} with a standard deviation of 1.0 Pg C y^{-1}) fail to reproduce any cases where methane oxidation in soil reaches a 2.0‰ change in the $\delta^{13}C_{pc}$ value. Therefore, best estimates of methane release rates are inconsistent with methane oxidation in soil pore spaces as the mechanism responsible for the oberserved values of

$\Delta CIE_{pc\text{-}som.}$ Methane injection rates an order of magnitude faster are required to explain the observations.

The CO_2 produced from methane oxidation is incorporated in $\delta^{13}C_{pc}$ assuming no change to $\delta^{13}C_{om}$. In reality, the decomposition of methanotrophs may also push $\delta^{13}C_{om}$ to more negative values as methanotroph biomass is added to the organic matter, therein decreasing $\Delta CIE_{pc\text{-}som}$. The relative extent to which methanotrophic activity affects $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ is a function of the carbon-use efficiency of the microbes (i.e. how much carbon from the methane is incorporated into biomass and how much is respired as CO_2). Indeed, the first sensitivity test ($MC_{meth\text{-}ox}$) works under the assumption that oxidation of methane in soil porespace does not influence $\delta^{13}C_{SOM}$, so the bias does potentially overestimate $\Delta CIE_{pc\text{-}om}$. However, a majority of simulations still fail to reproduce the observed $\Delta CIE_{pc\text{-}om}$ despite this overestimation. As a result, leaving out the effect of methanotrophs on SOM reinforces the conclusions as a conservative estimate. Because simulations of changes in respiration rate in the second sensitivity (MC_{resp}) test do not consider oxidation of methane in soil porespace, the effect is a non-issue in those cases too. Saturation of hydroxyl radicals in the troposphere and stratosphere in the atmosphere is not considered in the model, which could potential cause an underestimation of methane oxidation rates in soil and thus an underestimation of $\Delta CIE_{pc\text{-}om.}$ However, saturation of hydroxyls would need to account for approximately an order of magnitude increase in soil pore space oxidation to significantly change the results of the sensitivity test ($MC_{meth\text{-}ox}$). For example, in an injection of

~3000PgC injection over 100 years, the model assumes only 10% of atmospheric methane is oxidized in soil. If such an increase were to overload the oxidative capacity of the atmosphere, a much larger fraction of methane could diffuse into soil resulting in temporarily large spikes in oxidation rates. Calculating the input required to saturate OH^- radicals in both the troposphere and stratosphere is complex, especially given that production of CO from oxidation further saturates available OH (Isaken & Hov 1986). We can however, conclude that with a lack of complete saturation of stratospheric and tropospheric oxidative capacity, that oxidation of atmospheric methane diffusing into soil pore space is likely insufficient as the sole, or even primary mechanism responsible for the observed magnitude of $\Delta CIE_{pc\text{-}om.}$

Part II: *Effects of Elevated Respiration Rates on* $\delta^{13}C_{ped}$

The second sensitivity test (MC_{resp}) treats the prior for soil respiration rates as an independent variable. In this sensitivity test, the mechanism for methane oxidation in soil

is turned off, and the only difference between paired runs is the range of the flat

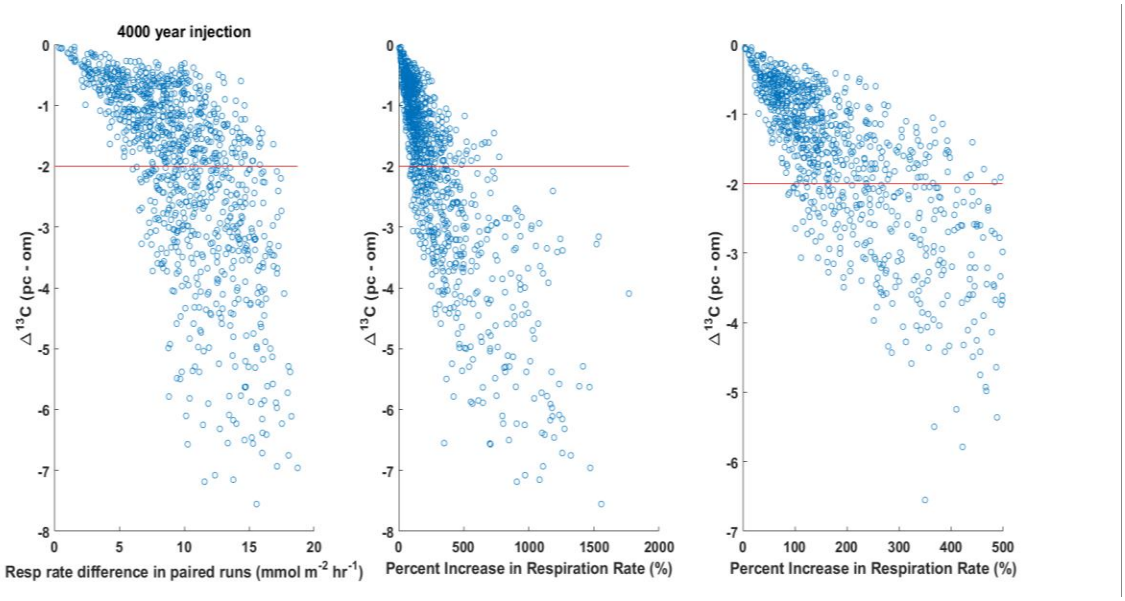

Figure 6: Excursion differences as a function of respiration rate (both absolute and relative). The first simulations to reproduce the observed difference do not occur until approximately a doubling of respiration.

distribution for soil respiration rates. Again, this respiration rate is the sum of both root respiration and microbial decomposition; whereas the first sensitivity test (*MC_{meth}-ox)* keeps the total soil respiration the same with the exception of incorporating an additional component of respiration in the form of methanotrophic activity. The soil respiration rate in the first of each paired run is kept at 0.1 – 10 mmol/m^2/h as in the previous test. The respiration rate in the second simulation in each pair samples from a flat distribution of 10 - 20 mmol/m^2/h while maintaining all other parameters in the previous run. Results are provided in terms of both an absolute and factor change in respiration rates. The minimum respiration rate required to produce a 2.0‰ difference consistent with observed records occurs at a respiration rate increase of 6.2 mmol/m2/h and an 87% increase in respiration

rates (i.e. $\frac{Resp\ PETM - Resp\ prePETM}{Resp\ prePETM} \times 100 = 87\%$). Additionally, 40.6% of simulations produced a respiration at or greater than the observed difference in $\Delta CIE_{pc\text{-}om}$. The mean for all $\Delta CIE_{pc\text{-}om}$ values was also $\mu = 2.0‰$ with $\sigma = 1.51‰$.

IV: Conclusions

Despite maintaining broad, conservative estimates for sampling distributions of unknowns, oxidation of methane in soil pore space is unlikely to be the primary cause of discrepancy in excursion magnitudes between $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$. Even with a 100-year release of ~3000PgC, less than 10% of simulations resulted in a $\Delta CIE_{pc\text{-}om}$ equal to or exceeding the 2‰ observed difference. Moreover, no simulations reached the observed difference when constraining the maximum carbon release to 3.0 Pg C y^{-1} or less.

It is likely that injection of carbon into the atmosphere occurred in pulses, some of which have exceeded a 1.1 or 3.0 Pg C y^{-1} upper limit. Still, given a relatively consistent discrepancy between $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ throughout the main body of the CIE, oxidation of methane in soil pore space remains an implausible explanation without a sustained release of methane more than an order of magnitude larger than a proposed 1.1 Pg C y^{-1} upper limit (Zeebe et al. 2016). Oxidation of methane in soil pore space causing the POE however, is harder to dismiss. Indeed, the mechanisms behind the difference in $\delta^{13}C_{pc}$ and $\delta^{13}C_{om}$ need not be the same between the POE and CIE. Conclusive data detailing the CIE_{om} for the POE has not been established, but the POE is characterized by two trends in the $\delta^{13}C_{pc}$ that warrant more consideration of methane oxidation as a possible cause. The CIE_{pc} is approximately 2.0‰ less during the POE than during the main PETM CIE. If we assume no change in $\delta^{13}C_{om}$ during the POE, there must be a mechanism that independently causes

a depletion in $\delta^{13}C_{pc}$ without affecting the $\delta^{13}C_{om}$. Furthermore, the highest methane flux into soil is expected near the beginning of the CIE because methane oxidizes quickly, but the resulting CO_2 is consumed slowly by silicate weathering, resulting in a CIE that is substantially longer than the duration of methane release. POE resulting from methane oxidation in soil would also be consistent with the rapid recovery observed in $\delta^{13}C_{pc}$, as pedogenic carbonate would cease to incorporate the depleted carbon as soon as atmospheric methane returned to prePETM levels. Still, given that a 30 Pg C y^{-1} (i.e. ~100-year release) produced less than 10% of simulations that reproduced observed excursions with conservative priors, it seems unlikely that the POE was primarily a product of methane oxidation in soil porespace. Evidence for methane release exceeding 3.0 Pg C y^{-1} during the POE, and a demonstrated small shift in $\delta^{13}C_{om}$ from prePETM values during the POE would be needed to substantiate such a claim.

Alternatively, a doubling in respiration rates can reproduce $\Delta CIE_{pc\text{-}om}$ values consistent with observations. Simulations centered on a release of 0.3 Pg C y^{-1} resulted in 40.6% of simulations surpassing the threshold. The observed difference was reproduced with a respiration change as small as 6.2 mmol/m^2/h and a percent increase in respiration of 87%. Respiration rates may increase as a result of increased CO_2 fertilization, temperature or moisture. We can look back to the geologic record to determine what evidence exists for these different potential causes.

The effect of temperature on SOM decomposition is typically isolated and quantified in terms of a van't Hoff Q_{10} value, the factor by which the rate increases with a 10ºC rise in temperature (Davidson and Janssens 2006). Most studies suggest a Q_{10} of ~2 for rates of SOM decomposition (Townsend et al. 1995, Rustad et al. 2001). A 10ºC warming is the upper-limit for the PETM, and warming is not thought to have peaked early within the PETM despite $\Delta CIE_{pc\text{-}om}$ existing even in the POE (Zachos et al. 2008, Bowen et al. 2015). Moreover, Q_{10} values are not applicable for thousand-year time scales. Q_{10} temperature dependencies are based on rates of decomposition of existing organic carbon and do not incorporate significant changes to carbon fluxes or cycling that occur as a result of ecosystem and vegetation change on longer time scales (Davidson et al. 2006, Lützow & Knabner 2009).

Furthermore, past experimental work demonstrates that warming and CO_2 fertilization can increase soil carbon input and turnover rates of SOM (MacDonald et al. 1995). A lack of organic matter increase throughout PETM paleosol records across terrestrial sites has been interpreted as the balancing of increased organic input during the PETM with an increase in SOM turnover (Bowen et al. 2004). Increased input from litter decomposition causes a decrease in $\delta^{13}C_{pc}$ and has no effect on $\delta^{13}C_{om}$, whereas increases in turnover could cause an increase in $\delta^{13}C_{om}$ and an increase in $\delta^{13}C_{pc}$. Given increases in both variables, $\Delta CIE_{pc\text{-}om}$ and CIE_{om} could not be fully accounted for without including additional ^{13}C-depletion in organic matter (Bowen et al. 2004). The same study suggested that an increase in relative humidity of at least 20% was required to simulate enough productivity and ^{13}C-depletion

in organic matter to reproduce $\Delta CIE_{pc\text{-}om}$, especially given additional hypothesized ^{13}C-enrichment due to transpiration stress at elevated temperatures during the PETM. This is consistent with increases in precipitation and subsequent increases in humidity, rather than CO_2 fertilization or increases in temperature, being the driving factor behind $\Delta CIE_{pc\text{-}om}$. In summary, it is difficult to explain respiration rate increase primarily as a function of increasing temperature and CO_2 given the difficulty in reconciling hypothesized PETM temperature increase with hypothesized Q_{10} values, CIE_{om}, and trends in organic matter composition in paleosol records.

More evidence for precipitation increase throughout the PETM exists at several mid-latitude sites (Kraus & Riggins 2007). Several studies characterize the onset of the PETM at Bighorn Basin with a marked transient decrease, followed by a steady increase in humidity as evidenced by changes in paleoflora, more poorly drained paleosols in younger samples, and discrepancies between excursion magnitudes between pedogenic carbonate and marine proxies (Wing et al. 2005, Kraus & Riggins 2007, Bowen et al. 2004). A more general increase in precipitation at Bighorn Basin is also consistent with climate modeling results for the PETM (Winguth et al. 2010, Koch et al. 2003, Shellito et al. 2003). An initial decrease in precipitation would hypothetically result in lower respiration rates, and thus would lower S(z) due to water stress at the onset of the PETM. The transient increase in water would cause an increase in respiration rates in well drained, dry soils. If we assume exceptionally low humidity and respiration in Bighorn at the onset (Kraus & Riggins 2007), even a small, transient increase in respiration could induce a large relative increase in soil

respiration rates, pushing $\delta^{13}C_{ped}$ values to more negative values compared to the prePETM. Such speculation would also need to be explained in the context of the PETM as a whole, where low moisture levels play a secondary role in lessening the negative excursion at the beginning of the PETM given low respiration, and slowing the return to prePETM $\delta^{13}C_{ped}$ values as Bighorn Basin increases in humidity.

Long term increases in respiration as a result of precipitation are also consistent with northward range extension of PETM flora at mid-latitudes (Wing et al. 2005). Increases in precipitation could potentially result in ecosystem change from prePETM to PETM at each site. Axhandle was likely an arid ecosystem (Bowen and Bowen 2008) while Tendruy and Bighorn were likely temperate forest (Domingo et al. 2009) during the PETM. For Tendruy and Bighorn, if mean annual differences in soil respiration across ecosystems were analogous to modern day, a 1.87x increase in respiration rate is equivalent to a transition from temperate grassland to a temperature forest, with annual soil respiration rates at 442 ± 78 and 647 ± 51 gC m^{-2} y^{-1} respectively (Raich & Schlesinger 1992). A doubling is also equivalent to a transition from desert scrub to temperate grassland with annual soil respiration rates at 224 ± 38 and 442 ± 78 gC m^{-2} y^{-1} respectively (Raich & Schlesinger 1992). The biggest inconsistency with this hypothesis exists at Tendruy, where there is hypothesized dry and arid conditions throughout the PETM, though there is evidence for seasonally wetter conditions during months without calcium carbonate formation (Schmitz and Pujalte 2003). A record of increased erosion of soils in the area is not consistent with a change in flora, as any long-term increase in steady precipitation rates should have

resulted in dense vegetation limiting, rather than exacerbating erosion rates. It is possible though, that precipitation was delivered primarily through storms in which case increased precipitation is not predicated on a lack of erosion. Overall, increased precipitation and subsequent increases in respiration rates are consistent with floral records, terrestrial proxies, and model results across a majority of terrestrial sites. More diverse and resolved geographic data is needed to confirm the extent to which precipitation driven increases in soil respiration rates can explain discrepancies in the magnitude of CIE recorded in soil carbonates and soil organic carbon across the PETM.

V: References

Zeebe, Richard E., Andy Ridgwell, and James C. Zachos. "Anthropogenic carbon release rate unprecedented during the past 66 million years." *Nature Geoscience* (2016).

Zeebe, Richard E., James C. Zachos, and Gerald R. Dickens. "Carbon dioxide forcing alone insufficient to explain Palaeocene–Eocene Thermal Maximum warming." *Nature Geoscience* 2.8 (2009): 576-580.

Stocker, Thomas F., ed. *Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, 2014.

Hesselbo, Stephen P., et al. "Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal)." *Earth and Planetary Science Letters* 253.3 (2007): 455-470.

Abels, Hemmo A., et al. "Terrestrial carbon isotope excursions and biotic change during Palaeogene hyperthermals." *Nature Geoscience* 5.5 (2012): 326-329.

Tipple, Brett J., et al. "Coupled high-resolution marine and terrestrial records of carbon and hydrologic cycles variations during the Paleocene–Eocene Thermal Maximum (PETM)." *Earth and Planetary Science Letters* 311.1 (2011): 82-92.

Cotton, Jennifer M., et al. "Positive feedback drives carbon release from soils to atmosphere during Paleocene/Eocene warming." *American Journal of Science* 315.4 (2015): 337-361.

McInerney, Francesca A., and Scott L. Wing. "The Paleocene-Eocene Thermal Maximum: A perturbation of carbon cycle, climate, and biosphere with implications for the future." *Annual Review of Earth and Planetary Sciences* 39 (2011): 489-516.

Rumpel, Cornelia, and Ingrid Kögel-Knabner. "Deep soil organic matter—a key but poorly understood component of terrestrial C cycle." *Plant and Soil* 338.1-2 (2011): 143-158.

Schubert, Brian A., and A. Hope Jahren. "Reconciliation of marine and terrestrial carbon isotope excursions based on changing atmospheric CO_2 levels." *Nature communications* 4 (2013): 1653.

Bowen, Gabriel J., et al. "A humid climate state during the Palaeocene/Eocene thermal maximum." *Nature* 432.7016 (2004): 495-499.

Dickens, Gerald R., et al. "Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene." *Paleoceanography* 10.6 (1995): 965-971.

Jones, T. Dunkley, et al. "A Palaeogene perspective on climate sensitivity and methane hydrate instability." *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*368.1919 (2010): 2395-2415.

Sluijs, A. *et al*. Environmental precursors to rapid light carbon injection at the Palaeocene/Eocene boundary. *Nature* 450, 1218–1221 (2007).

Dickens, Gerald R. "Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor." *Earth and Planetary Science Letters* 213.3 (2003): 169-183.

Magioncalda, Roberto, et al. "Paleocene-Eocene carbon isotope excursion in organic carbon and pedogenic carbonate: Direct comparison in a continental stratigraphic section." *Geology* 32.7 (2004): 553-556.

Dickens, Gerald R. "Down the Rabbit Hole: Toward appropriate discussion of methane release from gas hydrate systems during the Paleocene-Eocene thermal maximum and other past hyperthermal events." *Climate of the Past* 7.3 (2011): 831-846.

Cicerone, Ralph J., and Ronald S. Oremland. "Biogeochemical aspects of atmospheric methane." *Global biogeochemical cycles* 2.4 (1988): 299-327.

Roslev, Peter, Niels Iversen, and K. A. J. Henriksen. "Oxidation and assimilation of atmospheric methane by soil methane oxidizers." *Applied and Environmental Microbiology* 63.3 (1997): 874-880.

Bowen, Gabriel J., et al. "Two massive, rapid releases of carbon during the onset of the Palaeocene-Eocene thermal maximum." *Nature Geoscience* 8.1 (2015): 44-47.

Bowen, Gabriel J., and Brenda Beitler Bowen. "Mechanisms of PETM global change constrained by a new record from central Utah." *Geology* 36.5 (2008): 379-382.

Schmitz, Birger, and Victoriano Pujalte. "Sea-level, humidity, and land-erosion records across the initial Eocene thermal maximum from a continental-marine transect in northern Spain." *Geology* 31.8 (2003): 689-692.

Dickens, Gerald R. "The potential volume of oceanic methane hydrates with variable external conditions." *Organic Geochemistry* 32.10 (2001): 1179-1193.

Schmidt, Gavin A., and Drew T. Shindell. "Atmospheric composition, radiative forcing, and climate change as a consequence of a massive methane release from gas hydrates." *Paleoceanography* 18.1 (2003).

Ehhalt, D. H., and U. Schmidt. "Sources and sinks of atmospheric methane."*Pure and Applied Geophysics* 116.2-3 (1978): 452-464.

Dörr, Helmut, Luisa Katruff, and Ingeborg Levin. "Soil texture parameterization of the methane uptake in aerated soils." *Chemosphere* 26.1 (1993): 697-713.

Jackson, R_B, H. A. Mooney, and E-D. Schulze. "A global budget for fine root biomass, surface area, and nutrient contents." *Proceedings of the National Academy of Sciences* 94.14 (1997): 7362-7366.

Cerling, Thure E. "The stable isotopic composition of modern soil carbonate and its relationship to climate." *Earth and Planetary science letters* 71.2 (1984): 229-240.

Cerling, T. E. "Stable carbon isotopes in palaeosol carbonates."*Palaeoweathering, palaeosurfaces and related continental deposits* (1999): 43-60.

Diefendorf, Aaron F., et al. "Global patterns in leaf ^{13}C discrimination and implications for studies of past and future climate." *Proceedings of the National Academy of Sciences* 107.13 (2010): 5738-5743.

Panchuk, K., A. Ridgwell, and L. R. Kump. "Sedimentary response to Paleocene-Eocene Thermal Maximum carbon release: A model-data comparison." *Geology* 36.4 (2008): 315-318.

Zeebe, R. E. LOSCAR: long-term ocean-atmosphere-sediment carbon cycle reservoir model v2.0.4. *Geosci. Model Dev.* **5**, (2012): 149–166.

Bowen, Gabriel J., and James C. Zachos. "Rapid carbon sequestration at the termination of the Palaeocene-Eocene Thermal Maximum." *Nature Geoscience* 3.12 (2010): 866-869.

Breecker, D. O., Z. D. Sharp, and L. D. McFadden. "Atmospheric CO_2 concentrations during ancient greenhouse climates were similar to those predicted for AD 2100." *Proceedings of the National Academy of Sciences* 107.2 (2010): 576-580.

Hilting, Anna K., Lee R. Kump, and Timothy J. Bralower. "Variations in the oceanic vertical carbon isotope gradient and their implications for the Paleocene-Eocene biological pump." *Paleoceanography* 23.3 (2008).

Pearson, Paul N., and Martin R. Palmer. "Atmospheric carbon dioxide concentrations over the past 60 million years." *Nature* 406.6797 (2000): 695-699.

Royer, Dana L., Robert A. Berner, and Jeffrey Park. "Climate sensitivity constrained by CO_2 concentrations over the past 420 million years." *Nature* 446.7135 (2007): 530-532.

Pagani, Mark, et al. "An ancient carbon mystery." *Science* 314.5805 (2006): 1556.

Zeebe, R. E. Time-dependent climate sensitivity and the legacy of anthropogenic greenhouse gas emissions. *Proc. Natl Acad. Sci. USA* 110 (2013): 13739–13744.

Gaudry, A., Polian, G., Arduoin, B. and Lambert, G. "Radon-calibrated emissions of CO_2 from South Africa." *Tellus, 42B (1990): 9-19.*

Dorr, H. & Munnich, K.O. "222Rn flux and soil air concentration profiles in West Germany. Soil 222Rn as tracer for gas transport in the unsaturated soil zone." *Tellus, 42B (1990): 20-28.*

Breecker, D. O., et al. "Deep autotrophic soil respiration in shrubland and woodland ecosystems in central New Mexico." *Ecosystems* 15.1 (2012): 83-96.

Le Mer, Jean, and Pierre Roger. "Production, oxidation, emission and consumption of methane by soils: a review." *European Journal of Soil Biology* 37.1 (2001): 25-50.

Brook, George A., Michael E. Folkoff, and Elgene O. Box. "A world model of soil carbon dioxide." *Earth Surface Processes and Landforms* 8.1 (1983): 79-88.

Franzluebbers, K., A. J. Franzluebbers, and M. D. Jawson. "Environmental controls on soil and whole-ecosystem respiration from a tallgrass prairie."*Soil Science Society of America Journal* 66.1 (2002): 254-262.

Isaksen, Ivar SA, and Øystein Hov. "Calculation of trends in the tropospheric concentration of O_3, OH, CO, CH_4 and NO_x." *Tellus B* 39.3 (1987): 271-285.

Domingo, Laura, et al. "The Paleocene–Eocene Thermal Maximum record in the organic matter of the Claret and Tendruy continental sections (South-central Pyrenees, Lleida, Spain)." *Earth and Planetary Science Letters* 281.3 (2009): 226-237.

Davidson, Eric A., and Ivan A. Janssens. "Temperature sensitivity of soil carbon decomposition and feedbacks to climate change." *Nature* 440.7081 (2006): 165-173.

Davidson, Eric A., Ivan A. Janssens, and Yiqi Luo. "On the variability of respiration in terrestrial ecosystems: moving beyond Q10." *Global Change Biology* 12.2 (2006): 154-164.

Townsend, Alan R., et al. "Soil carbon pool structure and temperature sensitivity inferred using CO_2 and $^{13}CO_2$ incubation fluxes from five Hawaiian soils." *Biogeochemistry* 38.1 (1997): 1-17.

Rustad, Lindsey E., Thomas G. Huntington, and Richard D. Boone. "Controls on soil respiration: implications for climate change." *Biogeochemistry* 48.1 (2000): 1-6.

Turner, Sandra Kirtland, and Andy Ridgwell. "Development of a novel empirical framework for interpreting geological carbon isotope excursions, with implications for the rate of carbon injection across the PETM." *Earth and Planetary Science Letters* 435 (2016): 1-13.

Wing, Scott L., et al. "Transient floral change and rapid global warming at the Paleocene-Eocene boundary." *Science* 310.5750 (2005): 993-996.

Kraus, Mary J., and Susan Riggins. "Transient drying during the Paleocene–Eocene Thermal Maximum (PETM): analysis of paleosols in the Bighorn Basin, Wyoming." *Palaeogeography, Palaeoclimatology, Palaeoecology* 245.3 (2007): 444-461.

Winguth, A., et al. "climate response at the paleocene-eocene thermal maximum to greenhouse gas forcing-a model study with CCSM3." *Journal of Climate* 23.10 (2010): 2562-2584.

Koch, Paul L., et al. "Carbon and oxygen isotope records from paleosols spanning the Paleocene-Eocene boundary, Bighorn Basin, Wyoming." *SPECIAL PAPERS-GEOLOGICAL SOCIETY OF AMERICA* (2003): 49-64.

Shellito, Cindy J., Lisa C. Sloan, and Matthew Huber. "Climate model sensitivity to atmospheric CO_2 levels in the Early–Middle Paleogene." *Palaeogeography, Palaeoclimatology, Palaeoecology* 193.1 (2003): 113-123.

Chen, Quansheng, et al. "Effects of water content on soil respiration and the mechanisms." *Acta Ecologica Sinica* 23.5 (2002): 972-978.

MacDonald, Neil W., Donald R. Zak, and Kurt S. Pregitzer. "Temperature effects on kinetics of microbial respiration and net nitrogen and sulfur mineralization." *Soil Science Society of America Journal* 59.1 (1995): 233-240.

Brook, George A., Michael E. Folkoff, and Elgene O. Box. "A world model of soil carbon dioxide." *Earth Surface Processes and Landforms* 8.1 (1983): 79-88.

Cotton, Jennifer M., and Nathan D. Sheldon. "New constraints on using paleosols to reconstruct atmospheric pCO_2." *Geological Society of America Bulletin* 124.9-10 (2012): 1411-1423.

Von Lützow, Margit, and Ingrid Kögel-Knabner. "Temperature sensitivity of soil organic matter decomposition—what do we know?" *Biology and Fertility of Soils* 46.1 (2009): 1-15.

Raich, James W., and Christopher S. Potter. "Global patterns of carbon dioxide emissions from soils." *Global Biogeochemical Cycles* 9.1 (1995): 23-36.